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Evidence for the formation of a protective silica layer on the surface of POSS-Kapton®-PIs upon exposure to AO was found in X-Ray Photoelectron Spectroscopy (XPS) studies of POSS-Kapton®-PIs flown on the Materials International Space Station Experiment (MISSE1), and in separate studies of POSS-Kapton®-PIs exposed to AO in a ground-based facility. To directly compare the effect of AO on Kapton H®, SiO_2 coated Kapton HN®, and 8.75 weight % Si_8O_{11} cage "main-chain" POSS-Kapton®-polyimide (8.75 wt % Si_8O_{11} MC-POSS-PI), these materials were exposed to AO, scratched, and exposed to a second equivalent AO fluence. The erosion of the three materials, inside and outside of the scratched area, was monitored by stylus surface profilometry. The results of this study indicate that the POSS Kapton® PI reproducibly eroded about 200 nm before forming a silica layer. A thin film of 7 wt % Si_8O_{11} survived a 3.9 year flight on the MISSE1, on the International Space Station which resides at 500 km in LEO. The effects of temperature, physical property characterizations, and the MISSE1 flight will be discussed.

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Self-Passivation of POSS-Kapton-Polyimides in The Presence of Atomic Oxygen (Preprint)

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INTRODUCTION

Kapton[®] polyimide (PI) is used extensively on spacecraft as a flexible substrate for solar arrays because of its strength, temperature stability, insulation properties, UV stability, IR transparency, low solar absorptance and superior optical properties. It is also a component of spacecraft multilayer insulation blankets that thermally insulate to keep electronics and mechanical parts of the craft within the temperature design limits. [1]

It has been well established that polymeric materials undergo severe degradation in low Earth orbit (LEO), mainly due to the high concentration of atomic oxygen and its reactivity with organic materials.[2-10] Materials in LEO are also exposed to solar radiation, thermal cycling which can range from -50 ˚C to 150 ˚C, and bombardment by low and high-energy charged particles.[11]

AO in LEO impacts materials with a collision energy of 4.5-6 eV.[12-14] This O-atom translational energy can overcome many reaction barriers and facilitates the degradation of Kapton[®]. The silicon-oxygen bond energy is 8 eV, and this bond is intact after AO exposure. For this reason, Kapton[®] is typically coated with silica to impart resistance to AO. Imperfections in the silica layer created during the deposition process, or from impacts encountered during flight, lead to exposed Kapton[®]. It has been shown by de Groh et al that when protective aluminim coatings over Kapton are damaged in LEO, AO erodes the polymer matrix in a manner that creates burrowed out cavities. Computer simulations have shown that these cavities are created due to AO that ricochets in eroded spaces before reacting, causing a burrowing effect.[2]

The presence of Si and O in the polyimide polymer matrix leads to the formation of a protective silica layer on the polyimide surface when the POSS-Kapton[®] mix material reacts with AO. Polyhedral oligomeric silsesquioxane (POSS) is a Si and O cage-like structure surrounded by tailorable organic groups, which can be polymerizable. POSS diamines have been polymerized into the Kapton polyimide (PI) backbone creating nanodispersed Si and O in the polymer matrix. Our data indicates that upon AO exposure of POSS-PI films, the surface organic material erodes, while the atomic oxygen reacts with the nanodispersed POSS to form a silica passivation layer, therefore imparting remarkable AO resistance with minor effects in the storage modulus, glass transition temperature, and coefficient of thermal expansion.[15]

Evidence for the formation of a protective silica layer on the surface of POSS-Kapton[®]-PIs upon exposure to AO was found in X-Ray Photoelectron Spectroscopy (XPS) studies of POSS-Kapton[®]-PIs flown on the Materials International Space Station Experiment (MISSE1), and in separate studies of POSS-Kapton[®]-PIs exposed to AO in a ground-based facility. To directly compare the effect of AO on Kapton H[®], SiO_2 coated Kapton HN[®], and 8.75 weight % Si_8O_{11} cage "main-chain" POSS-Kapton[®]-polyimide (8.75 wt % Si_8O_{11} MC-POSS-PI), these materials were exposed

to AO, scratched, and exposed to a second equivalent AO fluence. The erosion of the three materials, inside and outside of the scratched area, was monitored by stylus surface profilometry. The results of this study indicate that the POSS Kapton[®] PI reproducibly eroded about 200 nm before forming a silica layer. A thin film of 7 wt % Si_8O_{11} survived a 3.9 year flight on the MISSE1, on the International Space Station which resides at 500 km in LEO. The effects of temperature, physical property characterizations, and the MISSE1 flight will be discussed.

EXPERIMENTAL

Synthesis of POSS-Polyimide Copolymers

Polyimides with the same chemical formula as Kapton[®] were synthesized by condensation polymerization of 4,4´-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in an N,N´-dimethylacetamide (DMAc) solvent [15, 16]. A POSS dianiline monomer (Figure 1) with two 1-(4-aminophenyl)-pendant groups and eight cyclopentyl pendant groups was synthesized using a procedure described by Feher et al. in 2003 [17]. Using this monomer, POSS-polyimide copolymers, shown in Figure 1, were synthesized with POSS loadings corresponding to 0, 5, 10, 20, and 25 wt%, which correspond to Si_8O_{11} cage loadings of 0, 1.75, 3.5, 7.0, and 8.75 wt %.[18] "Side-chain"-POSS (SC-POSS) monomer was synthesized by Wright, et al. [19] from which 3.5, 7.0 wt % Si_8O_{12} cage SC-POSS-PIs were synthesized in the same manner as described above. All poly(amic acids) were cured to POSS-PIs as previously reported. [18]

Exposure of POSS-Polyimides to Low Earth Orbit

MC-POSS-Kapton[®]PIs containing 0, 1.75, and 3.5 wt % Si_8O_{11}, were cast and cured onto 1 inch wide circular aluminium substrates. The sample thickness was not measured prior to flight. MC-POSS-Kapton[®]PIs are generally thicker towards the outer area after cure. The materials were flown in LEO on the International Space Station as part of the MISSE1. The samples were flown in Passive Experiment Container 1 (PEC 1), in Tray 1, developed by NASA Langley Research Center (LaRC), and were assigned numbers 38, 39, 40. Prior to flight, the samples were held into place in the tray by a top plate with open circles to expose the samples. The top plate also protects the outer area from exposure to the space environment.

The flight was launched on August 10, 2001 and was retrieved after 3.9 years in LEO as described at http://misse1.larc.nasa.gov/. The samples were exposed to all aspects of the LEO environment including AO and UV light. The step height difference between the masked (unexposed) outer ring and the neighbouring exposed sample area was measured in twelve places by profilometry. The surface atomic composition of the samples was determined by XPS.

AO Exposure of POSS-Polyimides

Ground-based POSS-PI sample exposures to AO were performed with a pulsed AO beam, operating at a repetition rate of 2 Hz and containing hyperthermal O-atoms that were generated by combining oxygen with 7 Joules per pulse CO_2 from a laser-detonation source [20-25]. The hyperthermal beam contains neutral O-atoms and molecular oxygen, with an ionic component of 0.01%. The mole fraction of AO in the beam was above 70 % and, for some exposures, above 90 %. Kinetic energies of the fast O-atoms in the beam can range from 2 to 15 eV, with the average being about 5.2 eV. Prior to exposure, samples were covered with a stainless steel mesh disk in order to mask areas and achieve AO exposed and unexposed areas. The O-atom fluence was on the order of 10^{20} O-atoms cm^{-2} for all experiments. All samples in this work were handled in ambient air after exposure and prior to etch depth determination by profilometry, surface topography, and surface chemistry measurements.[24]
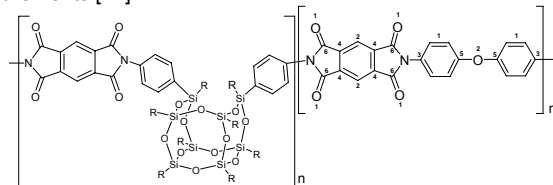

Figure 1. The structure of MC-POSS-Polyimide. R = cyclopentyl.

Surface Characterization of Scratched POSS-Polyimides

Three samples each of Kapton H[®], 8.75 % Si_8O_{11} MC-POSS PI, and silica-coated Kapton HN[®] (provided by Astral Technology Unlimited, Inc. Lot No. 00625-007, with a 130 nm SiO_2 coating) were exposed to 100k pulses of the beam, along with a Kapton H[®] standard. After the first exposure, the etch depths of the screened samples were measured. A set of unscreened samples underwent surface measurements. The third set of samples was scratched. For each sample, one approximately 40 µm wide and 1µm deep scratch was made with a diamond-tipped scribe, and two approximately 20 µm wide and 1µm deep scratches were made with a razor blade. All scratches were measured by profilometry (with a 5µm radius probe tip). Screens were placed over the scratched samples and these samples were exposed to additional 100k shots of the hyperthermal AO beam. Profilometry was used to measure step height differences between exposed and unexposed areas and to profile each scratch in AO exposed and unexposed areas.

XPS data was obtained with the use of non-monochromatized Mg Kα radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Scanning electron microscopy (SEM) was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector, at Edwards AFB, as previously reported. [18] SEM images of MISSE-flown samples were taken similarly, at Montana SU.

Physical Properties Characterization of POSS-Polyimides.

Polyimide samples were analyzed by a DMTA V from TA Instruments using a 5 ºC/min temperature ramp from room temperature to 500 ºC and a tensile geometry.[18] Measurements of the coefficient of thermal expansion (CTE) were taken on a thermo mechanical analyzer (TMA 2940) from TA Instruments with a film fiber attachment, in a nitrogen atmosphere. The cured films were cut into 15mm by 3mm samples, the force applied was 0.05N & 0.10 N, and the sample was heated at 5 °C/min. The CTE was calculated as $\alpha = (\Delta L \times K)/(L \times \Delta T)$ where L = length, K = a cell constant, T = temperature °C. Test variability was +/- 2.306 ppm/ °C based on five Kapton H[®] tests.

The Effect of Temperature on Erosion of POSS-Polyimides by a Hyperthermal O-Atom Beam.

The erosion of 0 wt %, 3.5 wt % and 7.0 wt % Si_8O_{11} POSS-polyimides exposed to a hyperthermal O-atom beam has been studied at 25 ºC, 100 ºC, 150 ºC, 220 ºC, and 300 ºC. Two samples of each type of material were exposed simultaneously. One of each sample type was covered with a screen during exposure. Each exposure was to 50,000 pulses of the hyperthermal O-atom beam, and included a "screened" Kapton H[®] reference sample. The O-atom fluence was on the order of 10^{20} O-atoms cm^{-2}. The nominal O-atom translational energy of each exposure was 5.2 eV, and the O/O_2 ratio in the beam was 0.65:0.35. For the 25 ºC exposure, the films (which were not cast on substrates) were placed in the sample holder. For the higher temperature exposures, the films were cast on germanium discs that were in contact with a controlled heating block during the exposures, and were equilibrated to the desired temperature.

RESULTS AND DISCUSSION

Most of the knowledge of the properties of POSS-PIs has been gained by their exposure to a ground-based simulated LEO environment. The AO exposure of 0, 3.5, 7.0, 8.75 wt % Si_8O_{11} MC-POSS-PI (POSS "R" group is cyclopentyl) films was carried out in a simulated LEO environment where films of these materials were etched by exposure to a hyperthermal O-atom beam. The difference in etch depth between the eroded and stainless steel screen-protected areas of the samples, made it possible to calculate an AO reaction efficiency (R_e) or erosion rate of the material for a given AO flux.[2]

The AO reaction efficiency of the Kapton H[®] reference sample was used to calculate the Kapton[®] equivalent fluence and erosion yields of each sample exposure. For various exposures, [18, 26] the derivative functions indicated that the 3.5 and 7.0 wt % Si_8O_{11} POSS polyimide films reached erosion rates of 3.7 and 0.98%, respectively, of the erosion rate for Kapton H[®] after 395,000 beam pulses (8.47 x 10^{20} atoms cm-[2]).[9, 10] 8.75 wt% Si_8O_{11} MC-POSS-PI samples had an erosion rate that was 0.3 percent of the erosion rate for Kapton H[®], and 1/3 of 7.0 wt % POSS-PI at a fluence of 8.5×10^{20} atoms cm^{-2}. These results support the formation of a passivating silica layer that is a result of the reaction of AO with nano-

dispersed POSS. A "self-passivation test" was carried out to better assess the protective silica layer formation witnessed by XPS of POSS-PIs. Kapton H[®], SiO_2 coated Kapton HN[®], and 8.75 wt % Si_8O_{11} MC-POSS-PI were exposed to equivalent AO fluences. The etch depth of the Kapton H[®] after the initial exposure was 7.0 ± 0.2 µm, indicating an O-atom fluence of 2.3 x 10^{20} O atoms cm^{-2}. The etch depth of 0.26 ± 0.15 µm of the 8.75 wt % Si_8O_{11} MC-POSS-PI film was difficult to measure since the overall etch depth was not much greater than the slight roughness caused by the exposure. For the SiO_2 coated Kapton HN[®] the etch depth was below the practical measurement limit of the profilometer and the sample surface appeared unaffected.

After the initial AO-exposure, Kapton H[®], SiO_2-coated Kapton HN[®], and 8.75 wt % Si_8O_{11} MC-POSS-PI were scratched and underwent a second exposure to 2.3 x 10^{20} O atoms cm^{-2}. SEM images of the results are shown in Figure 2. For the SEM image of Kapton H[®], the exposed region is in the left side of the image and has a more roughened surface with a deepened scratched area. The etch depth of the Kapton H[®] sample outside of the scratch was about 5.5 µm. The unexposed scratch was 20 µm wide and 1µm deep, and increased in depth to 1.4 µm after the second exposure. The top of the SiO_2-coated Kapton HN[®] image was exposed to AO and only had erosion in the scratched area with unaffected neighboring silica-coated Kapton HN[®], demonstrating the effects of damage to silica coatings on Kapton[®]. Here the unexposed scratch was 20 µm wide and 1µm deep and the exposed scratch was 8 µm deep relative to the neighboring exposed surface, amounting to 7 µm of erosion in the scratch. 8.75 wt % Si_8O_{11} MC-POSS-PI was exposed to AO in the darkened upper right area in Figure 2c. A difference in step height between exposed and unexposed unscratched areas of the 8.75 wt % Si_8O_{11} MC-POSS-PI was < 200nm and is not visible by microscopy. In Figure 2c, the scratch was 35 µm wide and 1.4 µm deep unexposed and about 1.8 µm deep after AO exposure. This result indicates that 8.75 wt % Si_8O_{11} MC-POSS-PI experienced about 400 nm of erosion inside the scratch during AO exposure. In comparison, Kapton H[®] eroded about 5 µm inside and outside the scratch, plus Kapton H[®] eroded an additional 0.200 µm in the scratch during exposure. These results are summarized in Table 1.

The results of the study of the effect of temperature on AO erosion of POSS-polyimides show that polyimide and POSS-PIs experience increasing erosion with increasing temperature. For each temperature, the etch-depths of the POSS-PIs divided by the etch depth of Kapton H[®] are given in Table 2. The erosion of the 0 wt % POSS-PI exhibited the strongest temperature dependence, with the etch depth increasing by a factor of about 3.6 from 25 ºC to 300 ºC. The 3.5 wt % and 7.0 wt % Si_8O_{11} POSS-PIs showed less temperature dependence in their erosion. The etch depths of these samples increase by factors of 2.2 and 2.4, respectively, with the increase from 25 ºC to 300 ºC, and the uncertainty in the measurements may bringthese factors closer.
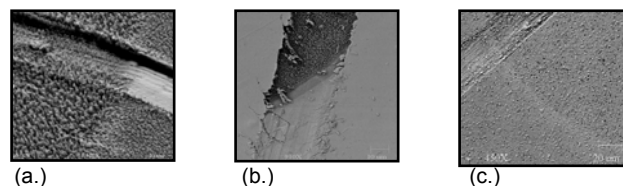

(a.)   (b.)   (c.)

Figure 2. SEM images of results from a self-passivation experiment. (a.) Kapton H[®], (b.) SiO_2 coated Kapton HN[®] (Provided by Astral Industries Inc.), and (c.) 8.75 wt % Si_8O_{11} cage MC-POSS-PI. Samples were exposed to 2.3 x 10^{20} atoms/cm^2, scratched, covered by a wire screen and exposed again to 2.3 x 10^{20} atoms/cm^2. The area covered by the wire screen was (a.) the right side, (b.) the bottom portion, and (c.) the left side.

Table 1. Self-Passivation Experiment Erosion Depths

Material	Kapton H[®]	SiO_2-coated Kapton HN[®]	8.75 wt % Si_8O_{11} MC-POSS PI
After 1st exposure.	5.5 µm	~ 0 µm	~ 0.200 µm

After 2nd exposure. Outside of scratch.	5 μm	~ 0 μm	~ 0 μm
After 2nd exposure. Inside of scratch.	5 μm	7 μm	~ 0.200 μm

Table 2. The Ratio of Etch Depths for Polyimide, and 3.5 wt % and 7.0 wt % Si_8O_{11} MC-POSS-polyimides to Kapton H® After Exposure to a Hyperthermal O-atom Beam at Five Temperatures.

Sample Temperature	Polyimide (PI)/ Kapton H® (μm)	3.5 wt % MC-POSS-PI/ Kapton H® (μm)	7.0 wt % MC-POSS-PI/ Kapton H® (μm)
300 ºC	3.30 ± 0.20	0.40 ± 0.06	0.21 ± 0.05
220 ºC	2.16 ± 0.16	0.27 ± 0.06	0.23 ± 0.03
150 ºC	1.49 ± 0.08	0.28 ± 0.03	0.11 ± 0.02
100 ºC	1.15 ± 0.11	0.23 ± 0.02	0.12 ± 0.02
25 ºC	0.91 ± 0.08	0.18 ± 0.02	0.086 ± 0.02

The results show that although POSS-PIs have increased erosion with temperature, they erode less than their no-POSS analogous. In most cases, a doubling of the POSS content from 3.5 wt % to 7.0 wt % Si_8O_{11}, causes the etch depth to decrease by about half. The O-atom fluences used in this study are at least half of those used in other work with these materials. It has been seen that at higher O-atom fluences, at room temperature, the erosion of polyimide increases linearly with fluence while the erosion of POSS-polyimide increases by approximately the square root of the fluence. [18, 26] Hence, it is expected that the higher fluence exposures and elevated temperatures, a more marked reduction in erosion yields for the POSS-polyimides compared to the erosion yields for the polyimide and Kapton H® films is expected.

The physical properties of POSS-PIs have been discussed previously.[15] The glass transition temperatures (Tg) were as follows: 420 ºC for 0 % POSS-PI, 394 ºC for 3.5 % Si_8O_{11} MC-POSS-PI, 390 ºC for 7 % Si_8O_{11} MC-POSS-PI, 383 ºC for 8.75 % Si_8O_{11} MC-POSS-PI. A side-chain POSS (SC-POSS) monomer has been synthesized by Wright et al. [19] and was readily copolymerized to form POSS-PIs with POSS as a pendant group. In an AO exposure with a total fluence of 3.53 x 10^{20} O atomx/cm^{-2}, 7 % Si_8O_{12} SC-POSS-PI had an erosion yield that was 3.3 % of Kapton H®. In an AO exposure with a total fluence of 4.10 x 10^{20} O atoms/cm^{-2}, 7 % Si_8O_{11} MC-POSS-PI had an erosion yield that was 3.8 % of Kapton H®. These results indicate that MC- and SC-POSS-PIs have approximately equal AO resistance.

The sudden temperature changes experienced by materials in the LEO environment make the coefficient of thermal expansion (CTE) an important material property. The CTE values for several samples are shown in Table 4. The addition of POSS slightly increases the CTE, and a slight decrease is seen after exposure of the SC-POSS-PI to AO. The CTE of fused silica is about 0.55 (μm/m°C) [27, 28] and the CTE of the silica passivation layer formed on POSS-PIs in the presence of AO is expected be close to that of silica in value. This mismatch between the silica passivation layer and the underlying POSS-PI is likely to cause cracks in the silica. The self-passivating properties of the POSS-PIs are expected to form a silica passivation layer in the areas where cracks or damage have occurred, once again protecting the underlying POSS-PI.

Table 3. Coefficients of Thermal Expansion for POSS-PI films.

Sample	*CTE (μm/m°C)*
Kapton H®	30.25
0% POSS-PI	33.11
7 % Si_8O_{11} MC-POSS-PI	33.5
8.75 % Si_8O_{11} MC-POSS-PI	35
7 % Si_8O_{12} SC-POSS-PI	35.86
7 % Si_8O_{12} SC-POSS-PI exposed to AO†	33.64

*Test variability based on 5 Kapton H® tests = ± 2.306 ppm/ºC.
†2.3x10^{20} oxygen atoms cm^{-2}

MC-POSS-PI films were flown on MISSE1 at about 500 km for 3.9

years. Various images of the samples were taken throughout the flight which show that the 0 % POSS-polyimide was completely eroded in less than four months. The innermost portion of the retrieved samples were thinner indicating they experienced greater erosion than the portion closer to the unexposed (masked) area, and/or they were thinner in this center area before flight. The step heights from the unexposed area and the neighboring exposed portion of the sample were measured in 12 places around the circumference of the exposed sample area. From these measurements, it was determined that the thickness of the masked 0 % POSS-polyimide is 32.55 ± 0.87 μm. 1.75 % MC-POSS-PI showed some survival with a step height of 5.79 ± 1.31 μm between the exposed outermost portion and the masked area, although an inner portion of this sample completely eroded. 3.5 % MC-POSS-PI film remained throughout with a step height of 2.12 ± 0.34 μm from the outermost portion and the unexposed area. It was determined by XPS that the atomic percentages of the top 10 nm of both POSS-PI films were 34 % Si, 59 % O, and 7 % C for both the 1.75 and 3.5 wt% Si_8O_{11} MC-POSS-PI samples.

Table 4. MISSE1 Step Height Erosion Data in Microns.

Data From 12 Step Height Measurements.	0% POSS PI	5% POSS PI	10% POSS PI
Total average	32.6	5.8	2.1
Standard Deviation	0.9	1.3	0.3
*erosion 3.9 yr	240	5.8	2.1

*0 % POSS-PI total erosion estimated using an AO fluence, estimated for the total fliglht time, of 8 x 10^{21} atoms/cm^2.
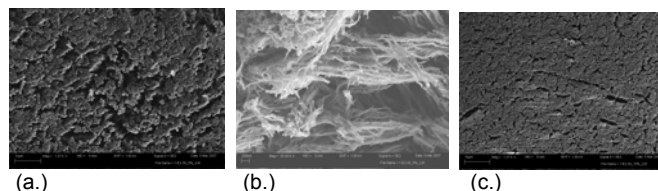

(a.)　　　　　(b.)　　　　　(c.)

Figure 3. Scanning Electron Micrographs of (a.) (b.) 1.75 wt % Si_8O_{11} MC-POSS-PI flown on MISSE1 and (c.) 3.5 wt % Si_8O_{11} MC-POSS-PI flown on MISSE1.

CONCLUSION

The incorporation of POSS nanostructures into polyimides has been shown to significantly extend the lifetime of these materials in LEO. Studies on the effect of a hyperthermal O-atom beam on POSS-PIs have shown the improved oxidation resistance imparted to polyimides by the addition of POSS. XPS data of both the AO-exposed and space-flown POSS-PI materials indicated that the improved oxidation resistance of these materials is due to a silica layer that is formed upon exposure of POSS-PIs to high incident fluxes of atomic oxygen.

A study of the response of scratched materials to AO showed that if a Kapton H® surface is scratched, the scratched material will erode at roughly the same rate as undamaged Kapton H®. A SiO_2 coating of 130 nm protected underlying polyimide from AO attack, but after the coating was compromised, the exposed polymer eroded (during AO exposure) at approximately the same rate that uncoated Kapton® eroded. The 8.75 wt % Si_8O_{11} MC-POSS-PI experienced roughly 1 - 2 % the erosion yield of Kapton H® that was exposed to an equivalent amount of AO. This difference can be accounted for by the formation of a silica layer on the surface of the material during AO exposure. When this layer was removed by a scratch, newly AO-exposed material had the same low erosion yield, indicating that a silica passivating layer formed in the scratched area.

The CTE of POSS-PIs is similar to the CTE of commercial Kapton H®. A new SC-POSS monomer imparts about the same AO resistance to polyimides as the MC-POSS monomer. The CTE of SC-POSS-PIs were

determined before and after exposure to atomic oxygen, and are comparable to the values of these properties for Kapton H®.

Kapton-PI and POSS-Kapton-PIs were flown in LEO for 3.9 years. The polyimide sample completely eroded before 4 months, and a thin film of the 3.5 wt % Si_8O_{11} POSS-polyimide remained after the flight demonstrating the space-survivability of POSS-PIs. Higher loadings of POSS in the PI matrix are expected to give improved flight results.

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